

NOVEL APPROACH TO COAL LIQUEFACTION
UTILIZING HYDROGEN SULFIDE AND CARBON MONOXIDE

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INTRODUCTION

All coal liquefaction processes involve thermal cracking of weak bonds in coal to form radical fragments which are stabilized by abstracting hydrogen atoms from a donor solvent. The activity of the hydrogen donor solvent is maintained by further hydrogenation of a recycled fraction. Thus, the costs of hydrogen comprise a major expense in any liquefaction process especially if pure H_2 is used. Hydrogen sulfide, a by-product of a negative value from the cleaning of natural gas, crude oil or coal, has been demonstrated to be a potential hydrogen source for a few chemical processes, such as selective reduction of NO_x to hydroxyl amine [1] and reduction of nitroaromatics to amines [2]. The effect of H_2S on coal liquefaction in the presence of hydrogen donor solvents and under H_2 atmosphere has been reported to increase the coal conversion to soluble products [3,4]. Hydrogen sulfide in these latter cases was not the main source of hydrogen but acted as a promoter in the presence of hydrogen donors and elemental H_2 . In order to utilize the inherent hydrogen value of hydrogen sulfide, we studied the effect of H_2S and CO on coal liquefaction in the absence of other hydrogen sources. A more detailed study of this chemistry was achieved by the use of coal tar, a material that contains many of the basic structural features of coal itself. The objective of this study has been to utilize low grade industrial hydrogen streams, particularly those produced via coal gasification which contain a large variety of impurities including H_2S , CO, CO_2 , COS and NH_3 . Utilization of the H_2S /CO from such dirty streams in the first stage of coal liquefaction will alleviate a number of expensive process steps in the cleaning of syngas.

EXPERIMENTAL

1. The coal liquefaction experiments were carried out in a 316 SS, 300 mL Magnedrive, packless, stirred autoclave (Autoclave Engineer, Inc.), fitted with a 1200 watt heating jacket. The coal was pulverized to -60 mesh and dried under nitrogen in a vacuum oven at 100°C. The coal sample (20 g), solvent (80 g of 1-methylnaphthalene or tetralin) and a catalyst (2 g), if required, were charged into the autoclave. The autoclave was flushed and pressure tested with nitrogen, then charged with 1655 kPa of H_2S (about 4.5 g) and to 6894 kPa with CO. The reaction was carried out at 400°C for 2 hours while stirring, then quenched utilizing a cold water cooling coil. The contents of the reactor were transferred into an extraction thimble and extracted with ethyl acetate for 24 hours. The thimble was dried in a vacuum oven and the weight of the residue

was determined. Conversion is defined as the percentage of the organic matter in coal that was converted to ethyl acetate-solubles and gases on a dry ash-free basis. The extract was stripped of ethyl acetate and the asphaltenes were precipitated by adding 800 mL of pentane. The sulfur contents of the asphaltenes were determined by Eschka method (ASTM D-271).

2. Coal tar treatment with H_2S and CO was carried out in the same manner as the coal liquefaction but without any solvents to avoid complications with the analytical procedure. Coal tar (80 g) was mixed with 5% presulfided Harshaw HT-400E catalyst ($Co-Mo-\gamma Al_2O_3$) and loaded into the autoclave prior to charging with H_2S (1655 kPa) and CO (6894 kPa). The autoclave was then heated at 400°C for 2 hours while stirring. Small aliquots of the product mixture were dissolved in $CDCl_3$, filtered, then subjected to both 1H -nmr and ^{13}C -nmr analysis. One experiment was carried out using 60% enriched ^{13}CO in a microreactor consisting of a 30 mL stainless steel vessel (Hoke) connected to a manifold and fitted with a magnetic stirrer and a heating jacket. The reaction was carried out at 350°C, 1655 kPa of H_2S and 5515 kPa of ^{13}CO for 6 hours. The contents of the vessel were extracted with $CDCl_3$, filtered and subjected to ^{13}C nmr. During the course of the coal tar treatment any hydrogen-containing solvents were carefully excluded.

3. Catalyst Preparation. A commercial sample of 13% MoO_3 and 3% CoO on γ -alumina was obtained from The Harshaw Chemical Company, Beachwood, Ohio. The pellets were ground to -60 mesh, heated to 500°C in a nitrogen stream, and then sulfided at 400°C with a 40% stream of H_2S in N_2 for one hour.

RESULTS

Utilization of the waste components from a coal cleaning process in the liquefaction of coal can only be achieved if H_2S , with other components, hydrogenates or serves as a radical trap during coal pyrolysis. The inherent hydrogen in hydrogen sulfide has now been shown to be capable of supplying the main source of hydrogen necessary for coal liquefaction. The coals were dried to avoid water that may act as a hydrogen source through the water-gas shift reaction. 1-Methylnaphthalene was used as a non-hydrogen donor dispersing medium. Catalysts used with certain runs were sulfided samples of $Co-Mo$ on $\gamma-Al_2O_3$ (Harshaw HT-400E). Liquefaction results of Illinois No. 6 Dean Mitchell coal are shown in Table 1. A comparison of the blank run in which coal was heated in 1-methylnaphthalene under nitrogen at 400°C and with H_2S treatment showed slight increase in conversion to ethyl acetate soluble products of 18% vs. 12.5% for the blank run indicating partial liquefaction using only H_2S . The sulfur content of the asphaltene fraction increased from 3.36% for the reaction under nitrogen to 6.34% when H_2S was used. The use of a mixture of H_2S and CO caused a threefold increase in conversion from 12.5% (Run 1) to 38.2% (Run 3). Sulfur content showed only a slight increase from 3.36% to 4.33%. Although the use of catalysts such as

sulfided Co-Mo on γ - Al_2O_3 (Run 4) or ammonium molybdate (impregnated on the coal, Run 5) did not cause significant change in conversion, it did decrease the sulfur content slightly. When a large excess of H_2S was used with the same amount of CO, a higher conversion was achieved with a slight increase in the sulfur content (Run 7).

Liquefaction of coal has been studied with mixtures of CO and H_2O by several groups with the main effort now involved in the COSTEAM process [5]. A comparison of $\text{H}_2\text{S}/\text{CO}$ versus $\text{H}_2\text{O}/\text{CO}$ was carried out. In the absence of a hydrogen donor solvent, $\text{H}_2\text{S}/\text{CO}$ was found to be more effective for coal liquefaction (38.2%) than $\text{H}_2\text{O}/\text{CO}$ (28%) under the same conditions (Runs 3 and 8).

The results of liquefying Illinois No. 6 Delta Mine coal in the presence of either an inert solvent (1-methylnaphthalene) or a hydrogen donor solvent (tetralin) are shown in Table 2. In agreement with previous data, the liquefaction in the presence of H_2S and CO in an inert solvent increased the conversion to 59.5% (Run 10) relative to a blank experiment (38.5% conversion, Run 9). The use of catalyst did not influence the conversion or the sulfur content. This indicated that the reaction of $\text{H}_2\text{S}/\text{CO}$ was either noncatalytic or catalyzed by the inorganic minerals in coal. The use of a hydrogen donor solvent gave a higher conversion and slightly lower sulfur content than the use of an inert solvent (Run 12 vs. Run 9). Furthermore, the use of $\text{H}_2\text{S}/\text{CO}$ enhanced the coal liquefaction in the presence of a hydrogen donor as evident from the results in Table 2.

Coal tar was used as a coal-like material in order to examine the nature of $\text{H}_2\text{S}/\text{CO}$ interaction on coal linkages. Although we do not imply that coal tar is a model for coal, it does contain many of the structural components in the original coal and has the added advantage of greater solubility in chloroform.

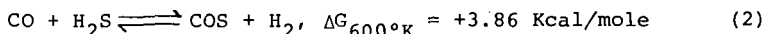
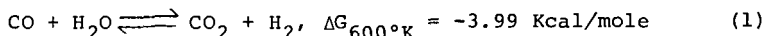
Coal tar samples were treated with $\text{H}_2\text{S}/\text{CO}$ in the presence of sulfided Co-Mo on Al_2O_3 catalysts under similar liquefaction conditions. Both ^1H and ^{13}C -nmr were used to evaluate the gross change in hydrogen and carbon distribution in coal tar as a result of $\text{H}_2\text{S}/\text{CO}$ treatment. Examination of the results in Table 3 demonstrated a substantial increase in the content of the aliphatic protons from 5.3% for the tar heated under nitrogen to 15.9% for the tar treated with $\text{H}_2\text{S}/\text{CO}$. A similar increase in the aliphatic carbon content from 4.4% to 6.6% was observed. The ^1H -nmr spectra of both nitrogen- and $\text{H}_2\text{S}/\text{CO}$ -treated coal indicated that the major change in the aliphatic hydrogen was due to functional aryl-methyl groups (singlets at δ 2.33-2.5 ppm) and the generation of ethylenic linkages between aromatic rings (singlets at δ 3.3 ppm) such as acenaphthene or dihydrophenanthrene structures. The appearance of aryl-methyl groups was quite intriguing since it indicated the possibility of methylating coal tar or coal using a mixture of $\text{H}_2\text{S}/\text{CO}$. The ^{13}C -nmr has substantiated this observation by indicating the appearance of singlet peaks around δ 22.0 and 30.3 ppm due to aryl-methyl and dihydrophenanthrene structures. The use of ^{13}CO and H_2S clearly showed the incorporation of $^{13}\text{CH}_3$ groups

as evident from the substantial increase in the aliphatic carbon, from 6.6% to 12.1% when CO or ^{13}C O was used respectively. The ^{13}C -nmr also indicated a major increase in the region of $\delta 18.5\text{--}22$ ppm indicative of aryl-methyl groups as a result of treating coal tar with ^{13}C O/ H_2S .

DISCUSSION

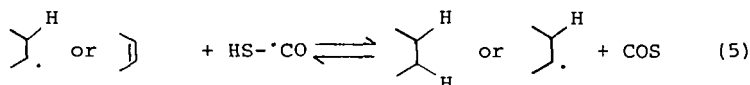
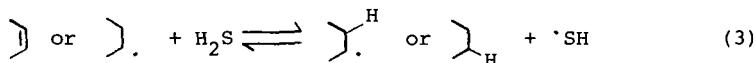
The above results show that the presence of CO with H_2S is required to achieve substantial hydrogenation and/or methylation of coal with H_2S . Hydrogen transfer to coal may involve nascent hydrogen or other similar intermediates that have been considered in CO/ H_2O reduction of coal. The weaker bond energy of H-S bonds in H_2S versus H-O bonds in H_2O undoubtedly provides one advantage for hydrogen transfer from H_2S . One must also consider a shift type reaction which can occur with H_2S /CO over sulfided catalysts to produce elemental H_2 [6].

While H_2S has a much lower heat of formation than water, a shift reaction for H_2S /CO is highly unfavorable as compared to the shift reaction for H_2O /CO.



A more likely mechanism for hydrogen transfer involves splitting of H_2S to give a hydrogen atom or abstraction of hydrogen atom from H_2S by the coal radical fragments followed by trapping the thiyl radical with CO to form a thioformyl radical. The latter is a better hydrogen donor than H_2S itself resulting in the formation of COS.

Scheme I



The ability of H_2S /CO to methylate aromatics only in the presence of a sulfided catalyst surface may also involve a thioformyl intermediate. We currently feel that thioformyl cations or radicals on an active metal sulfide surface attack aromatic rings which are electron rich. Subsequent hydrogenation of the thioformyl group appears to lead to the aryl-methyl product in a coal or coal tar. While methylation with H_2S /CO probably bears

resemblance to the formate mechanisms proposed earlier by Friedman, et al [7], further investigation of this area is necessary to make any accurate conclusions.

CONCLUSIONS

This investigation has shown that treatment of coal with a mixture of H_2S and CO allows the liquefaction of coal to an ethyl acetate soluble material. The interaction of H_2S/CO with coal results in both hydrogenation and methylation of coal fragments. While the mechanism has not been fully established, the ability of this reagent to solubilize coal in the absence of hydrogen and/or a donor solvent will allow reduction in the raw material cost of hydrogen in future liquefaction processes.

ACKNOWLEDGMENTS

The authors wish to acknowledge Mr. F. Worden for technical assistance and Mr. G. Babbitt for nmr analysis. We also acknowledge Professor M.J.S. Dewar for valuable discussions.

REFERENCES

1. C.T. Ratcliffe, U.S. Patent No. 4,115,523 (1979).
2. C.T. Ratcliffe and Geza Pap, submitted to J.C.S. Chem. Commun.
3. J.G. Gatsis, U.S. Patent No. 3,503,863 (1970).
4. R. Bearden, Jr. and C.L. Aldridge, U.S. Patents Nos. 4,077,867 (1978), 4,094,765 (1978) and 4,149,959 (1979).
5. H.R. Appell, E.C. Moroni and R.D. Miller, ACS Fuel Chem. Div. Preprints, Vol. 20, No. 1, 58 (1975).
6. K. Fukuda, M. Dokiya, T. Kameyama and Y. Kotera, J. Catal., 49, 379 (1977).
7. S. Friedman, H.H. Ginsberg, I. Wender and P.M. Yavorsky, "Continuous Processing of Urban Refuse to Oil Utilizing Carbon Monoxide"; The 3rd Mineral Waste Utilization Symposium, IIT, Chicago, IL, March 14-16, 1972.

TABLE 1. Dean Mitchell Coal Solubilization with H₂S, CO at 400°C for 2 hours

Run	Solvent	Reactants, Catalyst	Conversion (% daf)	Sulfur ^(a)
1	1-methylnaphthalene	N ₂	12.5	3.36
2	"	H ₂ S/N ₂	18.0	6.34
3	"	H ₂ S/CO	38.2	4.33
4	"	H ₂ S/CO, Co/Mo ^(b)	37.1	3.86
5	"	H ₂ S/CO, (NH ₄) ₂ MoO ₄ ^(c)	41.8	3.92
6	"	H ₂ S/CO, Co/Mo/K ₂ CO ₃ ^(b)	32.5	4.4
7	"	H ₂ S(25 g)/CO, Co/Mo ^(b)	46.6	4.85
8	"	H ₂ O/CO ^(d)	28.0	4.03

(a) Total sulfur in asphaltene.

(b) Sulfided Harshaw HT-400E. 3% Co, 12% Mo oxides on Al₂O₃.

(c) Wet impregnated on the coal followed by vacuum drying.

(d) H₂O quantity was 2.4 g, to provide same molar quantity as 4.5 g of H₂S. Pressure at ambient temperature was brought to 6894 kPa with CO.

TABLE 2. Delta Mine, Illinois No. 6 Coal Solubilization at 400°C for 2 hours

Run	Solvent	Reactants, Catalyst	Conversion (% daf)	Sulfur ^(a)
9	1-methylnaphthalene	N ₂	38.5	2.73
10	"	H ₂ S/CO	59.5	2.78
11	"	H ₂ S/CO, Co/Mo/K ₂ CO ₃ ^(b)	58.5	2.70
12	tetralin	N ₂	73.5	2.53
13	"	H ₂ S/CO, Co/Mo/K ₂ CO ₃ ^(b)	83.0	2.48

(a) Total sulfur in asphaltene.

(b) Sulfided Harshaw HT-400E. 3% Co, 12% Mo oxides on Al₂O₃.

TABLE 3. NMR Data of Coal Tar Reaction with
H₂S/CO

<u>Reactants</u>	<u>Aliphatic</u>		<u>Aromatic</u>	
	<u>H</u>	<u>C</u>	<u>H</u>	<u>C</u>
Coal tar, N ₂ (a)	5.3	4.4	94.74	95.6
Coal tar, H ₂ S, CO (a)	15.9	6.6	84.09	93.4
Coal tar, H ₂ S, 13CO (b)	12.7	12.1	87.17	87.9

(a) Reaction was carried out in 300 mL autoclave at 400°C, 6894 kPa ambient pressure for 2 hours in the presence of 5% Harshaw HT-400E sulfided catalyst.

(b) Reaction was carried out in 30 mL microreactor at 400°C, 5515 kPa ambient pressure for 6 hours in the presence of 5% Harshaw HT-400E sulfided catalyst.

PILOT UNIT EVALUATION OF EXXON DONOR SOLVENT (EDS) PROGRAM COALS. G. H. Anderson,
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4255, Baytown, Texas 77520.

Two Recycle Coal Liquefaction Units (RCLU's) are employed as a research and development tool to evaluate the performance of the Exxon Donor Solvent (EDS) coal liquefaction process with various program coals. These small (50 pounds-per-day and 100 pounds-per-day) integrated, continuous flow units with solvent recycle are used to evaluate new coals, investigate process modifications and conduct process variable studies. The RCLU's have been used to generate data for overall process yields and to provide information on operability trends for a variety of coals ranging in rank from lignitic through subbituminous to bituminous. We have found that the EDS process can be operated successfully throughout this range of coal rank. Optimum yields, and the conditions at which these yields are achieved, are strongly dependent on the specific coal. Recent process improvement operations have shown significant improvements in total liquid yield, as well as a lighter liquid product slate may be achieved. Operability trends are related to coal rank, with generally better operability obtained with higher rank coals. Yield and operability information from the RCLU's are used to select preferred operating conditions for the larger (one ton-per-day and 250 ton-per-day) pilot plants in preparation for future commercial operation.

EFFECTS OF SOLVENT HYDROGEN CONTENT IN THE SRC PROCESS. Ronald W. Skinner and Edwin N. Givens, Corporate Research and Development Department, Air Products and Chemicals, Inc., P. O. Box 538, Allentown, PA 18105.

Five coal-derived solvents containing between 6.2 and 9.5% hydrogen were compared as once-through SRC process solvents in a continuous flow unit equipped with a stirred tank reactor (CSTR). Gaseous hydrogen consumption varied inversely with the solvent hydrogen content. Coal conversion to pyridine soluble products was insensitive to solvent hydrogen; but the yield of toluene solubles decreased significantly with hydrogen-deficient solvents. The yields of liquid products and hydrocarbon gases were also reduced with hydrogen-deficient solvent. The approach to solvent equilibrium was examined in solvent recycle experiments using 8.7% H and 6.2% H starting solvents. After five passes, the recovered solvents had not reached equilibrium, as determined by differences in hydrogen content, fraction aromatic hydrogen, and average ring number. However, these differences in solvent composition did not affect the product yields.

CONTINUOUS HYDROLIQUEFACTION TESTS OF AUSTRALIAN BROWN COAL

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INTRODUCTION

The Australian state of Victoria possesses huge proven reserves (66.7×10^9 tonnes) of brown coal which have been shown (1-3) to be highly suitable for hydrogenation to liquid fuels. Previous ACIRL (3) batch autoclave tests on Victorian brown coal gave toluene-soluble liquid yields of 61% when hydrogenated in tetralin at 400°C for 4 hours at hydrogen pressure of around 21 MPa. Moreover, high yields of oil have been reported (4) for the hydrogenation of German brown coals (similar to the Victorian variety) in large-scale continuous operations.

Hydroliquefaction tests on a Victorian brown coal in ACIRL's 1 kg/hr continuous reactor unit are reported here. The unit and supporting equipment have been described earlier (5) with reference to black coal hydrogenation tests.

CONTINUOUS REACTOR OPERATIONS

The brown coal sample was from a steam-dried batch of run-of-mine brown coal then exposed to ambient room conditions for several hours. The coal was then crushed and screened to pass .075 mm and stored in polyethylene bags until required. Equilibrated moisture contents determined by the Dean and Stark (boiling toluene) method were in the range 11-16%.

The conditions under which these tests were run were -

Slurry solvent/coal ratio	1.68 - 2.0	: 1
Slurry feed rate	0.7 - 1.0	kg/hr
Hydrogen feed rate	88 - 92	g/h
Catalyst % Coal	0 - 4.3	
Temperatures:		
Preheater	25	- 450 C
Reactor	25	- 430 C
Preheater tube dimensions	6 - 25 m long	x 6 mm I.D. x 9.5mm O.D.
Reactor volume		3.5 L

Table 1 gives further run details.

The reactor internal configuration is shown in the figure. The reactor has been divided into three stirred compartments in an effort to increase the number of CSTR stages with minimal interstage backmixing, and thus to approach plug flow which is known to be more effective for a given reactor volume.

OPERABILITY

Feed slurry solvent/coal ratios were limited to above 1.68 : 1 as thicker slurries could not be pumped satisfactorily. At larger scales of operation it is likely that thicker slurries could more readily be handled. Accordingly, the data obtained at this small scale may be affected by the low feed slurry coal concentrations that could be achieved.

Product slurry let-down valves operating with pressure drops of up to 21 MPa down to atmospheric have survived longer (over 200 hours) in brown coal service than in black coal runs (50-100 hours). This is most likely the result of lower ash contents and lower percentages of hard macerals in brown coal.

Preheater tube blockages have been encountered in every run with brown coal. We observed that high temperatures tended to accelerate deposition of mineral matter and coke on the preheater wall. Deposition of solid coke-salt materials in preheaters also appears to be a problem for other workers in brown coal and lignite

hydrogenation. High levels of calcium have been qualitatively observed in some of our preheater solids. However the original deposit that eventually caused a blockage could not always be found because preheater contents tended to coke along the whole length when flow stopped. The original high-calcium deposit was then only locatable by laboriously cutting the whole preheater into many sections and examining each one individually.

RESULTS

Observed mass balances and oil yields are presented in Tables 2 and 3. Yield data corrected to 100% recovery for operationally stable runs 33, 44 and 45 are presented in Table 4. Overall recoveries for these runs were 95- 96%.

Because of the small scale of operations perfect mass balances were very difficult to achieve. Overall mass balances varied from 82% to 97%, the poorer mass balances being partly attributable to operational problems such as leaks, necessarily hasty remedial action to clear blockages in the feed slurry circulating system, and losses when discharging material in process in order to replace a blocked preheater.

Distillation mass balances (i.e. recovery of water, light oil, middle and vacuum distillates and distillation residue) were 95 - 98% of product slurry fed to the distillation equipment. Observed oil yields were corrected by assuming perfect recovery. Thus, observed oil yields in the range 31 - 44% for overall 95 - 96% recoveries are estimated to be in the range 42 - 55% assuming 100% recovery. We believe that the downside error is unlikely to be greater than 5%, that is the above oil yield range is unlikely to be less than 26 - 39%.

Observed distillate yields for runs with poor overall recoveries are unfortunately suspect. However, some conclusions can be drawn with reasonable certainty, namely:

- (a) Distillate oil yields of up to 55% can be obtained from this coal at conditions attainable in this bench unit.
- (b) Oil yields were higher when reactants flowed through both preheater and reactor (both at above 400°C) than through either alone. Some negative oil yields were observed probably as the result of degradation of solvent in the hot preheater.
- (c) Solids building up in the preheater tended to reduce liquid yields probably due to decreasing reaction volume.
- (d) Preheater deposits tended to form more rapidly at higher temperatures.
- (e) Added red mud and sulfur improved liquid yields slightly. Further verification of this effect is under way.

PRODUCT CHARACTERISTICS

Light oils (IBP - 200°C) were found to contain 19-37% paraffins, 19-27% naftenes, 26-50% aromatic hydrocarbons, and 9-14% oxygenated compounds, mainly phenols and ketones. This would suggest that substantial extraction and/or catalytic hydro-treatment would be required to produce a suitable feedstock for gasoline. By comparison light oils derived from black coals generally contain about half as much oxygenated compounds.

The heavier oils from which aliquots are used as recycle oil, contained substantial concentrations of heteroatoms of which phenolic hydroxyl groups accounted for 70-90% of the oxygen present. The concentration of saturated hydrocarbons increased up to 10% with succeeding recycle passes while aromatics and simple polar compounds remained approximately constant. Branched hydrocarbons were present in only very small amounts. After about 400 hours total operation, indications were that 30-40% of the original starting solvent components remained. In other words, the original starting solvent (mildly hydrogenated creosote) is fairly stable at these hydrogenation conditions and thus it merely becomes diluted with every succeeding recycle pass.

CONCLUSION

It is important to recognise that these data were generated on a small bench unit and are indicative of trends and likely ranges of oil yields. These runs have provided valuable experience enabling us to better plan future improvements to improve mass balances and yields. However, we believe that at this small scale the best recoveries achievable are 98% on feed slurry, that is 95-96% on feed coal.

ACKNOWLEDGEMENTS

Support was provided under the National Energy Research, Development and Demonstration Program administered by the Commonwealth Department of National Development and the Victorian Brown Coal Council. Permission by Mr. A.H. Hams, ACIRL's General Manager and Director of Research to present this paper is gratefully acknowledged. The assistance of J.F. Cudmore, R.E. Guyot, P.A. Bennett, R. Staker and co-operating ACIRL staff is also gratefully acknowledged.

TABLE 1.
Run Conditions

Runs	Duration h	Brown Coal feed kg	Starting Solvent	Solvent/ Coal Ratio	Catalyst % coal
33	98	25	100 % MHC	1.68 : 1	4.3
34-36	311	85	100% MHC then RS from previous runs	1.78 - 2.0 : 1	0 - 1.2
44A, B	100	30	49% MHC 51% RS from previous runs	1.80 : 1	4.0
45	106	35	100% RS from Run 44	1.80 : 1	4.0

MHC = mildly hydrogenated creosote
RS = recycle solvent
Catalyst = 75% red mud + 25% elemental sulfur.

TABLE 2.
Unit Configuration and Preheater Behaviour

Runs	Preheater			Reactor	
	Temperature C	Status	Time to block, h	Temperature C	Status
33	450	In	71	425	In
34A	450	In	-	-	Out
34B	450	In	89	425	In
35A	450	In	53	425	In
35B	450	In	26	-	Out
36A	450	In	-	-	Out
36B	450	In	50	370	In
36C	-	Out	-	425	In
44A	435	In	59	430	In
44B	410	In	-	430	In
45	410	In	86*	430	In

* Blockage cleared by imposed excess pressure drop.
All other blocked preheaters could not be cleared
and were therefore replaced.

TABLE 3.
Mass Balances and Yields

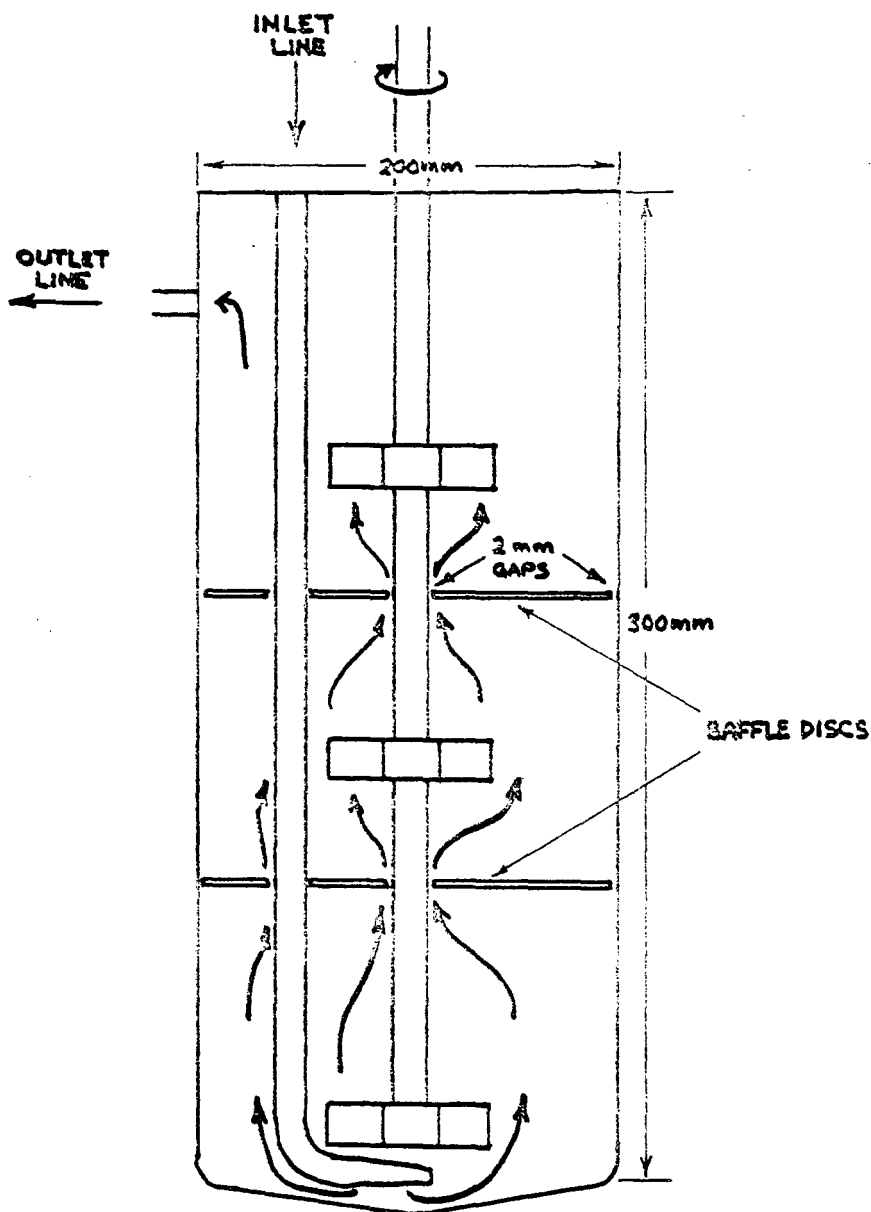
Run	Mass Balance Closure on Total Feeds (%)			Observed Distillate Yield % d.a.f. Coal
	Continuous Reactor	Distillation	Overall	
33	100.1	94.7	95	44
34A	85	97.9	83	-16
34B	84	97.6	82	- 5
35A	89	96.5	86	- 2
35B	95	98.7	94	3
36A	101.4	98.6	97	-11
36B	98.0	97.2	95	- 7
36C	89	98.2	87	11
44A	97.4	97.4	95	31
44B	97.6	97.4	95	38
45	98.3	97.8	96	32

TABLE 4.
Yields Corrected to 100% Recovery

Run	33	44A	44B	45
<u>IN</u>				
Coal (d.a.f.)	100	100	100	100
Hydrogen consumed	6	10	12	7
	<u>106</u>	<u>110</u>	<u>112</u>	<u>107</u>
<u>OUT</u>				
C ₁ - C ₄ hydrocarbons	13	17	13	11
CO, CO ₂	12	17	14	15
Heterogases	2	1	1	3
Generated Water	12	13	12	15
Light Oil (IBP - 200°C)	10	13	10	10
Middle Distillate (200 - 320°C)	28	25	29	22
Vacuum Distillate (320 - 550°C)	17	7	13	10
Distillation Residue (d.a.f.)	12	17	20	21
	<u>106</u>	<u>110</u>	<u>112</u>	<u>107</u>
Net distillate Oil Yield, % d.a.f. coal	55	45	52	42

REFERENCES

1. SINNATT, F.S., and G.E. BARAGWANATH (1938) "The Hydrogenation of Victorian Brown Coals" State Electricity Commission of Victoria (2nd Edition, 1974)
2. GUYOT, R.E. (1976) "Production of Synthetic Oil and Chemicals from Coal - Part 3 - Relationships between Coal Properties and Hydroliquefaction Potential" ACIRL Report P.R. 76-8.
3. GUYOT, R.E. (1978) "Influence of Coal Characteristics on the Yields and Properties of Hydrogenation Products" ACIRL Report P.R. 78-8.
4. KRÖNIG, W. (1977) "Kohlehydrierung (Erzeugen von Kohlenwasserstoffen durch Direkthydrierung)" Ch. 4 Georg Thieme, Stuttgart, 1977.
5. KELVIN, N.V.P. (1979) "Hydroliquefaction of Australian Coals" A.C.S. Div. Fuel Chem. Sept. 1979, Washington D.C.



Internal Configuration of Stirred Reactor

Disposable Catalysts for Coal Liquefaction

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The objective of DOE's Disposable Catalyst Program is to utilize the mineral matter in coal or other inexpensive naturally occurring ores as coal liquefaction catalysts which will substantially reduce hydrogen consumption and increase selectivity to liquids. Fundamental and applied research work performed in several laboratories has been coordinated into an integrated program. Research in the area of coal minerals has shown that pyrites and pyrrhotites are active and effective catalysts for the hydroliquefaction of coals exhibiting both hydrocracking and hydrogenation functionalities. Batch experiments have shown that pyrite or pyrrhotite addition improves coal conversion as well as product selectivity, i.e., a 5 wt% pyrite addition increases the conversion of coal to benzene solubles product equivalent to 25° C operating temperature increase and to distillate product equivalent to 20° C operating temperature increase.

Pyrites from various coals provide different levels of catalytic activity which are attributed to differences in morphologies of the pyrites and/or are related to different inherent surface area of the pyrites.

Pyrites from mineral deposits show in general lower catalytic activity than coal-extracted pyrites.

The catalytic role of coal mineral clays and their effect on the pyrite-pyrrhotite catalytic system is being studied.

THE MECHANISM OF HYDROGEN TRANSFER FROM DIALIN DONORS, D.H. Bass and P.S. Virk,
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We report experiments concerning the transfer of hydrogen from the two dihydronaphthalene isomers, namely Δ^1 -dialin and Δ^2 -dialin, to two polynuclear hydrocarbon acceptors, namely anthracene and phenanthrene. These substrates were chosen both to model some of the hydrocarbon moieties involved in coal liquefaction as well as to test our hypothesis that the hydrogen transfer occurs by a concerted pericyclic reaction. The Woodward-Hoffmann rules for orbital symmetry conservation then suggest that hydrogen transfer to anthracene should be thermally-allowed from Δ^2 -dialin but forbidden from Δ^1 -dialin; however hydrogen transfer to phenanthrene should be thermally-allowed from Δ^1 -dialin but forbidden from Δ^2 -dialin. The experiments were conducted in tubing bomb reactors in the temperature range 240 C to 430 C, at times from 5 to 960 minutes and donor-to-acceptor mol ratios from 0.25 to 16. Reactions were essentially first order in each of donor and acceptor, with second order rate constants, $\log_{10}k$ (liter/mol s) tabulated below:

Donor +	Δ^1 -dialin	Δ^2 -dialin	tetralin
Anthracene 300 C	-5.1	-3.0	-6.1
Phenanthrene 400 C	-4.0	-5.5	-5.7

The experimental results evidently accord with the theoretical predictions for a pericyclic hydrogen-transfer.

COMPARISON OF METHODS FOR THE DETERMINATION OF
ASPHALTENES, OILS AND INSOLUBLES - PART II

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INTRODUCTION

According to Sternberg et al., asphaltenes are high molecular weight compounds which affect the viscosity of products from coal conversion processes (10) and may be the intermediaries in the formation of oil from coal (3, 6, 12). Asphaltenes have traditionally been defined by their solubility properties. A knowledge of the concentration of asphaltenes in coal-derived oil is often helpful to the engineer in evaluating hydrotreating processes. Studies of coal hydrogenation at DOE's Pittsburgh Energy Technology Center (formerly Pittsburgh Energy Research Center, Bureau of Mines) over the years often depended on the determination of asphaltenes (5, 11, 12). However, there is no standard method for the determination of asphaltenes in the products from coal conversion, nor is there any known relationship between asphaltene values produced by the analytical methods currently in use. Therefore, one cannot with any degree of confidence compare the asphaltene content of coal derived liquid fuels that are analyzed by different methods. At present, every laboratory has developed its own procedure for determining asphaltenes in coal-derived materials.

In order to ascertain if the different methods used to determine asphaltenes in coal-derived materials produce significantly different results, a study was initiated at the Pittsburgh Energy Technology Center aimed at objectively comparing five different methods currently used to analyze such

materials for asphaltenes, oils and insolubles. Part I of the study involved the use of a hydroliquefaction product of intermediate asphaltene content as a test material and was reported previously (7). Part II of the study is reported herein and involves the use of a high asphaltene containing substance as the test material.

EXPERIMENTAL

The experimental methods used were the same as those employed in Part I (7). A solid product from the Solvent Refined Coal (SRC) plant of Fort Lewis, Washington was chosen for the "standard" material. A large sample of the SRC was provided by the Combustion Division at PETC and was subsequently ground to pass through a 60-mesh screen. After thorough mixing, the SRC was divided into five portions which were stored under nitrogen in sealed, dark glass bottles until used.

The analytical procedures used were outlined previously (7) and will be described in greater detail in a future publication.

Method A has been in use by the Analytical Chemistry Branch at PETC for years for routine, high volume work and requires only inexpensive equipment (5). No attempt is made to keep the sample or the various fractions from contact with the air since chemical characterization of the fractions was not a consideration in the design or use of this method.

Method B was developed in the Molecular Spectroscopy Branch at PETC to give rapid results with a small number of samples and to produce fractions for further study (8).

Method C was designed in the Process Sciences Division at PETC as a means of studying the conditions for precipitation of asphaltenes and for preparing fractions for further study (2, 9).

Method D was developed at ARCO as a means of preparing fractions for further study (4).

Method E was designed at EXXON Research and Engineering Company as a preparative method (1). Due to the limited amount of sample available and after consultations with the originators of the method, a 25 gram sample size was employed instead of the 50 gram sample originally specified.

RESULTS AND DISCUSSION

The results of the study are shown in Table 1. After replicating method C a number of times it became apparent that the results varied so widely that the method was not working well enough to warrant continued replication. It was concluded that the probable cause of the observed variation was the passing of fine particles through the extraction thimble in a non-reproducible way. The results for method C were therefore left out of Table 1.

The averages vary over almost a factor of 2 for insolubles and asphaltenes and almost a factor of 15 for the oils. The ranges for the relative standard deviations were 4 to 9% for the insolubles, 6 to 15% for the asphaltenes and 4 to 40% for the oils.

The sums of the average values of insolubles, asphaltenes and oils for methods B, D and E (the oils are calculated by difference in method A) add up to more than 100%. While the difference between the sums of the average values and 100% are not statistically significant at the 95% confidence interval for methods B and D (it is for method E), the fact that all three methods show sums of greater than 100% can be interpreted as evidence of solvent retention in the fractions (the use of nitrogen in these methods would make oxidation an unlikely explanation).

In order to determine in an objective manner if significant differences exist between the results obtained from the various methods, Student's "t" test was applied. The results obtained with methods A, B, D and E were compared two at a time and in all cases statistically significant differences were found.

Based on the experience gained during this study the analysts involved made estimates for each method of the elapsed time and man-hours necessary to complete a determination and of the expected production rate. They concluded that in all cases these were not as favorable as those for the medium asphaltene material in Part I of the study (7). The differences were mainly due to the difficulties encountered in removing solvents from the insoluble material and, in some cases, the oils.

CONCLUSIONS

This study has shown that materials high in asphaltenes are more difficult to analyze for their asphaltene content than materials of moderate asphaltene content. Indeed, one of the test methods failed completely to work with the test sample. As authors of the method report (9) successfully applying the method to an SRC-I material, it was concluded that our results were caused by either of two things. First, although the specifications spelled out in the method were met, the Soxhlet thimbles were obtained from a different manufacturer than used by the originators and therefore may have been of a different porosity allowing fine particles through. Second, the SRC used was different than that reported on and may have been ground to a different average particle size.

Four of the methods worked but were less precise, required more effort and produced analyses at a lower rate than they did with the more tractable medium asphaltene material. In spite of all the above, methods A, B, D and

E could be used to analyze high asphaltene materials but each will produce different results with the same material. Clearly a standard method is called for but whether one method can be devised that will be usable with coal derived materials of widely varying asphaltene content is problematical.

REFERENCES

1. Aczel, T., R. B. Williams, R. J. Pancirov, and J. H. Karchmer. Chemical Properities of SYNTHOIL Products and Feeds, Anal. Proj. Rept. BRD.1BA.76, EXXON Research and Engineering Company, Baytown, Texas.
2. Bockrath, B. C. PETC/DOE, personal communication, May 1977.
3. Husack, R. and C. Golumbic. J. Am. Chem. Soc. 73, 1567 (1951).
4. Kutta, H. W. and E. H. Burk. Investigations on the Nature of Preasphaltenes Derived From Solvent Refined Coal Conversion Products, Atlantic Richfield Company, Harvey Technical Center, 400 E. Sibley Boulevard, Harvey, Illinois.
5. Mima, M. J., H. Schultz, and W. E. McKinstry. Method for the Determination of Benzene Insolubles, Asphaltenes, and Oils in Coal-Derived Liquids, PERC/RI-76/6.
6. Pelipetz, M. G., E. M. Kuhn, S. Friedman, and H. H. Storch. Ind. & Eng. Chem. 40, 1259 (1948).
7. Schultz, H. and M. J. Mima. American Chemical Society, Division of Fuel Chemistry, Preprints of papers presented at Anaheim, California, March 12-17, 1978, Volume 23, No. 2, pp. 76-78.
8. Schweighardt, F. K. PETC/DOE, personal communication, January 1977.
9. Steffgen, F. W., K. T. Schroeder, and B. C. Bockrath. Anal. Chem 51, 1164 (1979).
10. Sternberg, H. W., R. Raymond, and F. K. Schweighardt, Science 188, 49 (1975).
11. Weller, S., M. G. Pelipetz, and S. Friedman. Ind. & Eng. Chem. 43, 1572 (1951).
12. Weller, S., op.cit., pp. 1575-79.

Table 1. Average of 20 replicate analyses of a sample of SRC.

<u>Method</u>	<u>% Insolubles</u> <u>± 1S</u>	<u>% Asphaltenes</u> <u>± 1S</u>	<u>% Oils</u> <u>± 1S</u>
A	37 ± 3	52 ± 3	12 ± 2
B	58 ± 5	43 ± 6	1.5 ± 0.6
C	<u>See Text</u>		
D	64 ± 3	27 ± 4	14 ± 2
E	49 ± 2	34 ± 2	22.0 ± 0.8